Characteristics and properties of rice starch films reinforced with palm pressed fibers

Phattaraporn, T., Waranyou, S., Fazilah, A. and Thawien, W.

Starch and Plant Fiber Research Unit (SPF-RU), Department of Material Product Technology, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand.
Food Technology Division, School of Industrial Technology Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

Abstract: The aim of this research has been to study if palm pressed fiber (PPF) can be used as reinforcement in rice starch (RS) films. The mechanical properties and water vapor permeability as well as thermal properties of RS films reinforced with 125, 177, 250 and 420 µm (mesh no. 120, 80, 60 and 40, respectively) of PPF fiber at 10 20 30 and 40% of starch were investigated. The impact of PPF content was more significant, overall the RS films properties than size of PPF. The results demonstrated that tensile strength and water vapor permeability of RS films increased with increasing PPF content concomitant with decreased in elongation at break and transparency. Addition of PPF fiber significantly increased RS film yellowness but decreased lightness of RS films. The thermal properties of RS films reinforced with PPF was investigated by TGA, DSC and DMTA. The thermal stability and glass temperature (Tg) shifted towards higher temperatures with increasing amount of PPF, which can be restriction of the mobility of starch chain due to the establishment of strong interactions between starch and PPF. Addition of 420 µm of PPF showed little better properties including mechanical and thermal properties as well as physical properties than 250,177 and 125 µm, respectively.

Keywords: Rice starch film, palm pressed fiber, reinforcement, mechanical properties, thermal properties

Introduction

The improper disposition of the enormous volume of petroleum-derived plastics in the environmental has led to environment pollution and raised much interest in edible and biodegradable films from nature polymers, the biodegradable and renewable resources (Lawton, 1996; Fishman et al., 2000). Usually biodegradable and edible films include lipids, proteins and carbohydrates such as cellulose, starch and there derivatives in their formulation (Rodriguez et al., 2006). Starch is one of the most studied and promising raw materials for the production of biodegradable plastics, which is a natural renewable carbohydrate polymer obtained from a great variety of crops. Starch is a low cost material in comparison to most synthetic plastics and is readily available. Starch has been investigated widely for the potential manufacture of products such as water-soluble pouches for detergents and insecticides, flushable liners and bags, and medical delivery systems and devices (Fishman et al., 2000). Rice is the most widely consumed basic food in the world. Each year over 500 million tons of rice is harvested, providing sustenance to many countries and people throughout the world. The unique properties of rice starches are found in its many varieties (Bourtoom and Chinnan, 2008). Rice starch and its major components, amylose and amylpectin, are biopolymers, which are attractive raw materials for used as barriers in packaging materials. They have been used to produce biodegradable films to partially or entirely replace plastic polymers because of its low cost and renewability, as well as possessing good mechanical properties (Xu et al., 2005). However, compared to the common thermoplastics, biodegradable products based on starch (Lourdin et al., 1995; Arvanitoyannis and Biliaderis, 1997; Garcia et al., 1999; Mali and Grossmann, 2003), unfortunately, still reveal many disadvantages such as low mechanical properties and efficient barrier against low polarity compounds (Kester and Fennema, 1986). The disadvantages
mainly attributed to the highly hydrophilic character of starch polymers (Santayanon and Wootthikanokkhan, 2003). To cope with these problems while persevering the biodegradability of the materials, one approach is the use of fibers as reinforcement for starch (Ma et al., 2008). Natural fiber-reinforced composites have many advantages such as light weight, reasonable strength and stiffness, renewable and biodegradable (Demir et al., 2006; Kunanopparat et al., 2008). Various types of fillers have been tested such as potato pulp based microfibrils (Dufresne et al., 2000; Dufresne and Vignon, 1998), bleached leaf wood fibers (Funke et al., 1998; Averous and Boquillon, 2004), bleached eucalyptus pulp fibers (Curvelo et al., 2001), wood pulp (De Carvalho et al., 2002), softwood aspen (Low et al., 2007), Jute, Hemp and flax fibers (Wollerdorfer et al., 2006) tunicin whiskers (Angles and Dufresne, 1998; Soykeabkaew et al., 2004; Park et al., 2006) and oil palm fibers (Sreekala and Thomas, 2003).

Oil palm empty fruit bunches are obtained after the extraction of oil from the seeds. Many million tons of empty fruit bunches are produced annually throughout the world, as an industrial waste by the oil mills, and left unutilized. This creates a good habitat for insects and pests, thereby causing severe environmental problems. Therefore, the utilization of this fiber as reinforcement in plastics has economical as well as ecological importance (; Rozman et al., 1996; Agrawal et al., 2000). However, the resulted polymer or plastic property reinforced with fiber was not only depends on type of fiber but also depends on the content and sizes of fibers (Herrera-Franco and Valadez-Gonzalez, 2005; Shih, 2007). In previous work (Bourtoom and Chinnan, 2008) a rice starch edible film was developed. It has been observed that the functional properties e.g., the film ductility and the barrier properties of rice starch film are generally poor. Beside, at the moment, there is very limit information on rice starch film reinforced with fiber. The objective of this work was to investigate the properties of rice starch films reinforced with palm pressed fibre. The effects of fiber content and fiber size on physical, mechanical and thermal properties were investigated.

Materials and Methods

Materials

Native rice starch (Thai Flower brand) used was obtained from Bangkok Starch Industrial Co. Ltd. and had a moisture content of about 14g/100g sample (determined in triplicate by vacuum drying at 70°C and < 1 mmHg pressure for 24 h, EYELA™, Model VOS-300VD, Japan) and peak viscosity (8g/100g sample solid) of 500 BU (Brabender unit, Model VISKOGRAPH, Germany). Native rice starch (Thai Flower brand) was obtained from Bangkok Starch Industrial Co. Ltd. Commercial grade sorbitol was obtained from Vidyasom Co. Ltd. (Thailand).

Preparation of palm presses fiber

Palm pressed fiber (PPF) were prepared by acid treatment (10% HNO₃) on dry base of palm pressed fiber at 90°C for 1 h, and bleaching the produced pulp using the sodium chloride bleaching method (Browning, 1967). Bleached palm pressed fiber was then size reduction and screened at 40 (420 µm), 60 (250 µm), 80 (177 µm) and 120 mesh (125 µm).

Film preparation

Starch solution with concentration of 3% (w/v) was prepared by dispersing rice starch in distilled water and heating the mixtures with stirring until it gelatinized (85°C for 5 min), and then cooling to 45±2°C. The solution was filtered through a polyester screen (mesh no.140 with mesh opening of 106 µm) by vacuum aspiration to remove any small lumps in the solution. Sorbitol was added (50% of the total solid weight). Subsequently, the PPF at various sizes (420, 250, 177 and 125 µm) and different contents (10, 20, 30 and 40% w/w of starch) were added and stirred for 20 min. After mixing, the mixer was degassed under vacuum cast onto flat, leveled non-stick tray to set. Once set, the tray were held at 55°C for 10 h undisturbed, and then cooled to ambient temperature before peeling the films off the plates. Film samples were stored in plastic bag and held in desiccators at 60% RH for further testing. All treatments were made in triplicate.

Film testing

Conditioning

All films were conditioned prior to subjecting them to permeability and mechanical tests according to the Standard method, D618-61 (ASTM, 1993a). Films used for testing water vapor permeability (WVP), tensile strength (TS), and elongation (E) were conditioned at 60% RH and 27±2°C by placing them in desiccators over a saturated solution of Mg(NO₃)₂.6H₂O for 72 h or more. For other tests, film samples were transferred to plastic bags after peeling and placed in desiccators.

Film thickness

Thickness of the films was measured with a precision digital micrometer (Digimatic Indicator, Mitutoyo Corporation, Japan) to the nearest 0.0001
(±5%) at five random locations on the film. Mean thickness values for each sample were calculated and used in water vapor permeability (WVP) and tensile strength (TS) calculations.

**Water Vapor Permeability (WVP)**

The gravimetric Modified Cup Method based on ASTM E96-92 (McHugh *et al.*, 1993) was used to determine the WVP of films. The test cups were filled with 20g of Silica gel (desiccant) to produce a 0% RH below the film. A sample was placed in between the cup and the ring cover of each cup coated with silicone sealant (high vacuum grease, Lithelin, Hannau, Germany) and held with four screws around the cup’s circumference. The air gap was at approximately 1.5cm between the film surface and desiccant. The water vapor transmission rates (WVTR) of each film were measured at 60±2% RH and 25±2°C. After taking the initial weight of the test cup, it was placed into a growth chamber with an air velocity rate of 125 m/min (Model KBF115, Contherm Scientific, Lower Hutt, New Zealand). Weight gain measurements were taken by weighing the test cup to the nearest 0.0001g with an electronic scale (Sartorious Corp.) every 3 h for 18 h. A plot of weight gained versus time was used to determine the WVTR. The slope of the linear portion of this plot represented the steady state amount of water vapor diffusing through the film per unit time (g/h).

The WVTR was expressed in gram units, per square meter, per day. Steady state over time (slope) yielded a regression coefficient of 0.99 or greater. Six samples per treatment were tested. The WVP of film was calculated by multiplying the steady WVTR by the film thickness and dividing that by the water vapor pressure difference across the film.

**Tensile Strength and Elongation at the Break (TS and E)**

Tensile strength was measured with a LLOYD Instrument (Model LR30K, LLOYD Instruments Ltd., Hampshire, England) as per ASTM D882-91 Standard Method (ASTM, 1993b). Ten samples, 2.54 cm x 12cm, were cut from each film. Initial grip separation and crosshead speed were set at 50mm and 50mm/min, respectively. Tensile strength was calculated by dividing the maximum force by the initial specimen cross-sectional area, and the percent elongation at the break was calculated as follows:

\[ E = 100 \times \frac{d_{\text{after}} - d_{\text{before}}}{d_{\text{before}}} \]

Where, \(d\) was the distance between grips holding the specimen before or after the break of the specimen.

**Color**

A CIE colorimeter (Hunter associates laboratory, Inc., VA, USA) was used to determine the film L*, a*, and b* color value \([L^* = 0 \text{ (black)} \text{ to } 100 \text{ (white)}; a^* = -60 \text{ (green)} \text{ to } +60 \text{ (red)}; \text{ and } b^* = -60 \text{ (blue)} \text{ to } +60 \text{ (yellow)}]\). The standard plate (calibration plate CX0384, \(L^* = 92.82, a^* = -1.24, \text{ and } b^* = 0.5\)) was used as a standard. Color (means of five measurements at different locations on each specimen) was measured on 10cm x 10cm segment of film. Total color difference \((\Delta E_{ab})\), hue angle (H), and chroma (C) were calculated using the following equation:

\[ \Delta L^* = L^* \text{ sample } - L^* \text{ standard}, \quad \Delta a^* = a^* \text{ sample } - a^* \text{ standard}, \quad \Delta b^* = b^* \text{ sample } - b^* \text{ standard} \]

\[ \Delta E_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \]

\[ C = [(a^*)^2 + (b^*)^2]^{0.5} \]

\[ H = \tan^{-1} \frac{b^*}{a^*} \text{ when } a^* > 0 \text{ and } b^* > 0 \]

\[ H = 180^o + \tan^{-1} \frac{b^*}{a^*} \text{ when } a^* < 0 \]

\[ H = 360^o + \tan^{-1} \frac{b^*}{a^*} \text{ when } a^* > 0 \text{ and } b^* < 0 \]

Prior to taking color measurements, film specimens were pre-conditioned at 60% RH and 27±2°C for 72 h.

**Transparency**

The transparency of films was determined using a UV-1601 spectrophotometer (Shimadzu, Kyoto, Japan). The films sample were cut into rectangles and placed on the internal side of spectrophotometer cell. The transmittance of films was determined at 600 nm as described by Han and Floros (1997). The transparency of the films was calculated as follows:

\[ \text{Transparency} = -\log \frac{T_{600}}{x} \]

Where \(T_{600}\) is the transmittance at 600 nm and \(x\) is the film thickness (mm).

**Thermogravimetric analysis (TGA)**

Thermogravimetric analysis was performed to study the degradation characteristic of the films. Thermal stability of each sample was determined using a (PerkinElmer, TGA7) with a heating rate of 10 °C/min in a nitrogen environment. It has a weighing capacity of 1.0 g. Samples were heated from room temperature to 500°C.

**Differential scanning calorimetry (DSC)**

The DSC analysis was determined using a modulated differential scanning calorimeter (PerkinElmer, DSC7) with refrigerator cooler. Calibration was based on pure indium and sapphire. An empty Aluminum pan was used as reference.
Samples (0.03 g) were scanned at a rate of 10 °C/min between temperature ranges of -50 °C to 220 °C. The glass transition temperatures were determined from the resulting thermograms as the midpoint between onset and end temperatures of step changes in heat flow observed during heating and identified as second-order transitions.

Dynamic mechanical thermal analysis (DMTA)

The small deformation analysis of the films was performed in tension in a dynamic mechanical thermal analyzer (Rheometric Scientific, DMTA V). The tested filmstrips were cut into small strips (20 × 5 mm) and clamped in the instrument with the initial grip separation 5.5 mm. The films were subjected to a sinusoidal strain on top of a static deformation. The testing was conducted at a constant frequency of 1 Hz and a strain of 0.02% and over a temperature range of 50 to 200 °C, at a heating rate of 5 °C/min. The measurements of each experimental point were done at least in triplicates. When dynamic mechanical spectroscopy is employed within the linear viscoelastic regime to determine Tg, the storage and loss modulus (E’ and E’’)) and loss tangent (tanδ = ΔE’/E’’) are measured as a function of temperature at a constant frequency and a selected heating or cooling rate.

Statistical analysis

A factorial design was used to characterize the composite films. Analysis of variance (ANOVA) was used to compare mean differences of the samples. If the differences in mean existed, multiple comparisons were performed using Duncan’s Multiple Range Test (DMRT).

Results and Discussion

Mechanical properties

The TS and E of the rice starch (RS) films reinforced with palm pressed fiber (PPF) or RS/PPF biocomposite films is depicted in Figure 1. The TS of RS films were affected by size and content of PPF. The results demonstrated that the TS of RS films enhanced as addition of PPF. This behavior was expected and was attributed to the resistance exerted by the fiber itself and due to 3D hydrogen bonds network formed between different components (Lu et al., 2006). Furthermore, increasing of fillers content from 0 to 40% of starch resulted in an increase of TS (Figure 1a), indicated that a high compatibility occurs between starch matrix and PPF fillers and the performances (e.g., mechanical properties) Besides, at lower fiber content dispersion of fiber is very poor so that TS will not occur properly. Similar results were observed by Sreekumar et al. (2007) and Sangthong et al. (2008). Size of PPF fillers also affected the TS of RS films; the result showed that, TS remarked increase as size of PPF fillers increase from 125 to 420 µm. According to the results, the maximum TS of RS films reinforced with 40% of starch at 420 µm (16.26 MPa) (Figure 1a). Regarding the tensile behavior of resole composites fiber size of 420 µm was found to be the optimum size for RS films. In the case of fibers smaller than this optimum size, the fibers will de-bond from the matrix resulting in weaker of composite. Ali et al. (2003) found that the strength efficiency factor and modulus efficiency factor of polycaprolactone (PCL) composites was obtained when longer fiber was applied. Besides, Dong et al. (1993) pointed out that short fiber act more like flaws in the structure of the matrix rather than as reinforcement agent, this could be the reason for the lower of tensile strength values. This result shows a reasonable agreement with experimental of Arbelaitz et al. (2006). Regarding the Elongation at Break (E), size of PPF did not significant effect on the E but there was affected by the PPF content; results showed that increases in PPF fillers from 0 to 40% of starch provided decrease in %E from 40.54% to 1.69% (Figure 1b). The experiments showed that TS and %E of RS/PPF films is almost inversely related.

Barrier properties

As a food packaging, film is often required to avoid or at least to decrease moisture transfer between the food and the surrounding atmosphere, and water vapor permeability should be as low as possible (Ma et al., 2008). The results demonstrated that RS films contained 40% PPF was broken during measuring the water vapor permeability, resulted from the occurring of brittle films. Hence, only 10-30% PPF was presented in this study. Water vapor permeability (WVP) of the composites decreased with the addition of PPF, and the highest occurred when no fiber was added (14.15 g.mm/m².day.kPa) but the lowest value (4.27 g.mm/m².day.kPa) being obtained with addition of PPF (Figure. 2), this results pointed out that water resistance of PPF was better than rice starch matrix. However, WVP of the RS films tended to increase as content of fibers increased (Figure 2). For example, WVP of the RS films increased from 4.33 g.mm/day.m².kPa to 10.60 g.mm/day.m².kPa when increasing the PPF content from 10 to 30% of starch at 420 µm of PPF (Figure 2). The addition of PPF probably introduced a tortuous path for water molecule to pass through (Kristo and Biliaderis, 2007). At a low content of filler, PPF dispersed well in the rice starch matrix,
Figure 1. Effect of size and content of PPF on tensile strength (A) and elongation at break (B) of RS films. Mean values with different letter are significantly different (p<0.05)
and blocked the water vapor. However, superfluous filler was easy to congregate and increased porous on films, which actually decreased the effective contents of fiber and facilitated the water vapor permeation (Ma et al., 2008). Additionally, as the fiber content increased the water absorption also increased due to the increased hydrophilic nature of the fibers. Moreover, large number of porous tubular structures present in fiber accelerates the penetration of water by the so-called capillary action (Sreekumar et al., 2007).

Similar trend was observed in for the composites prepared by Espert et al. (2004). Size of PPF fillers also affected the WVP of RS films, the result showed that, WVP tended to increase as size of PPF fillers decrease from 420 to 125 µm, because the small size of PPF increased the surface for contact the water in surrounding atmosphere. Espert et al. (2004) reported that the changes in WVP of composite films due to the effect of the filler added are highly dependent on the size and aspect ratio (width-to-height) of the filler. Besides, bigger size of fiber showed higher agglomerated and, probably, this fact diminished the effectiveness of fiber for WVP decrease.

**Color and transparency**

Color of the packaging is an important factor in terms of general appearance and consumer acceptance (Srinivasa et al., 2007). The results of the measurements performed on the RS film’s color were expressed in accordance with CIELAB system and the rectangular coordinates (L*, a* and b*) and the total color difference (ΔE*ab), hue angle and chroma were calculated. Figure 3 and 4 depicted results from the effect of size and content of PPF fillers on color (L*, a*, b*, ΔE*ab, chroma and hue angle) of RS films. These results showed that the content of PPF fillers significant effect on the color of RS films. The b* chroma and ΔE*ab values increased as content of PPF fillers increased from 10 to 40 % of starch concomitant with decreased in L*, a* and hue angle values. This indicated the decreasing lightness (L*) and increasing yellowness (b* and chroma) of film, possibly due to the PPF have white-yellowish color. Transparency of the films is also of importance in some instances, when used as packaging materials. Addition of PPF fiber into the RS films resulted in decrease their transparency. Rice starch film with out PPF fiber was the highest transparent. However, the lower transparency of the films was noticed when a greater amount of PPF was incorporated (Figure 5). The decrease in transparency could possibly arise from the light scattering from the retarding of light transmission of the PPF and RS/PPF films. At high level of PPF, the RS films demonstrated lower transparency than lesser PPF incorporation.

**Thermal properties**

TGA thermograms and the char yields (500 °C) of various samples under nitrogen are shown in Figure 6 and Table 1. The behavior of the char yield curves was similar in the composites (Figure 6). The fiber, even at low content (10% of starch, as shown in Figure 6), could improve thermal stability of RS films. The char yield of RS film was lesser (8.5%) than RS films reinforced with PPF (10.6-14.1%), resulting from the greater thermal stability of the PPF. By the reason

![Figure 2](image-url)
Figure 3. Effect of size and content of PPF on $L^*$ (A); $a^*$ (B) and $b^*$ (C) of RS films. Mean values with different letter are significantly different ($p<0.05$)
Figure 4. Effect of size and content of PPF on ∆E* (A); Hue angle (B) and Chroma (C) of RS films. Mean values with different letter are significantly different (p<0.05)

Figure 5. Effect of size and content of PPF on transparency of RS films. Mean values with different letter are significantly different (p<0.05)
of the mainly composition of PPF are cellulose that was strong structure. Therefore, addition of PPF into the RS films can be improved the thermal stability of RS films. It was found that the char yield of RS films was enhanced as PPF fillers content increased. For example, the char yield increased from 8.5 to 14.1% when increasing the PPF content from 0 to 40% of starch (Figure 6). These results indicated that fiber addition increased the thermal stability of RS films, which is in agreement with the results reported by Ruseckaite and Jimenez (2003) for composites with sisal fibers and PCL matrix. The results revealed that the composites, the moisture content mainly contributed to mass loss at the onset temperature, while for pure RS films the moisture content and the addition of plasticizer resulted in the mass loss. This difference was due to the good adhesion between RS films and fiber. The fiber component decreased the mass loss of plasticizer, therefore, the thermal stability of RS films was improved.

The DSC results, which showed that the presence of PPF increases the $T_g$ of the matrix, are in agreement with the water sorption experiments. Figure 7 shows the DSC curves in the temperature region of -50 to 220 $^\circ$C of the RS film and PPF/RS films. No endothermic peaks, assigned to the glass transition C of the RS films reinforced with PPF. No endothermic peaks, assigned to the glass transition temperature ($T_g$) of RS films. However, can be observed from the increasing endothermic heat flow when PPF was added into RS films. With the increase of PPF contents, the endothermic heat flow increased gradually, might be attributed to the occurrence of intermolecular interactions occurred between starch and PPF, which reduces the flexibility of molecular chains of starch (Lu et al., 2006). This behavior was already observed with different polysaccharides reinforced with cellulose fiber (Curvelo et al., 2001; Ma et al., 2005; Arbelaiz et al., 2006).

Table 1. Char yields of PPF, RS films and 10-40g /100 g of PPF (420 $\mu$m) reinforced RS films

<table>
<thead>
<tr>
<th>Fiber/Composite films</th>
<th>Char yield (g/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPF</td>
<td>22.80 ± 1.54</td>
</tr>
<tr>
<td>RS film</td>
<td>8.50 ± 1.25</td>
</tr>
<tr>
<td>RS film ± 10% PPF</td>
<td>10.63 ± 0.82</td>
</tr>
<tr>
<td>RS film ± 20% PPF</td>
<td>11.82 ± 1.06</td>
</tr>
<tr>
<td>RS film ± 30% PPF</td>
<td>13.54 ± 0.52</td>
</tr>
<tr>
<td>RS film ± 40% PPF</td>
<td>14.17 ± 1.03</td>
</tr>
</tbody>
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Figure 8 shows the temperature dependence of dynamic mechanical thermal analysis behaviors for the RS film and PPF/RS film. The storage modulus ($E'$) of the RS film and PPF/RS films as a function of temperature is given in Figure 8a. The storage modulus of the films was increased with increasing PPF content compared to the pure RS film. By incorporating PPF fillers of 0 to 30% of starch, the thermal stability shifts to higher temperature. This can be attributed to the strong interfacial interactions through hydrogen bonding between large specific surface of PPF and starch matrix (Angles and Dufresne, 2001).

Figure 8b shows the tan $\delta$ curves of the RS film and PPF/RS films as a function of temperature. The glass transition temperatures were estimated from the tan $\delta$ peaks. The RS film exhibits a $T_g$ transition at about 148 $^\circ$C. Additionally, the $T_g$ of thermoplastic starch depends on the plasticizer content and humidity conditions as well as the composition of starch (Alemdar and Sain, 2008). With increasing the PPF fillers content from 0 to 30% of starch, the tan $\delta$ peak shifts from 148 to 187 $^\circ$C, indicating that PPF fillers restrict molecular motions of starch, due to the strong interaction between starch and fillers (Park et al., 2002).

Conclusions

Palm Pressed Fiber (PPF) was used as a reinforced for RS film. The impact of PPF content was more significant, overall the RS films properties than size of PPF. The PPF/RS films increase in tensile strength (TS) but decrease in elongation at break of film. The incorporation of PPF into RS films provided the improvement of water resistance for the RS films. The improvement properties of the films can be attributed to the formation of rigid hydrogen bonded network of cellulose in the composite that is governed by percolation mechanism. Rice starch films filled with PPF showed better thermal stability than unfilled RS films, besides resulted from the restriction of the mobility of starch chain due to the establishment of strong interactions between starch and PPF. The results demonstrated that addition of 420 $\mu$m of PPF showed little better properties including mechanical and thermal properties as well as physical properties than 250, 177 and 125 $\mu$m.

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Figure 6. TGA thermograms of PPF, RS films and 10-40g /100 g of PPF (420 µm) reinforced RS films

Figure 7. DSC curves of PPF, RS films and 10-40g /100 g of PPF (420 µm) reinforced RS films

Figure 8. The dynamic mechanical behaviors of both (a) storage modulus (E’) and (b) loss factor (tan δ) as a function of temperature for of PPF, RS films and 10-30g /100 g of PPF (420 µm) reinforced RS films
References


